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Laser-ablated boron atoms react with methyl fluoride in an argon stream to form two major products, CH2BF and CHBF. In similar reactions of boron with methyl chloride and methyl bromide, both CH2BX and CHBX are also observed, as well as the primary insertion products, CH3BCI and CH3BBr, respectively. Infrared spectra of isotopic combinations of B and CH3X and desnity functional theory frequency calculations provide evidence for the product identification. Both products form via insertion into the C-X bond followed by loss of one or two H atoms for all reactions. Comparisons are made with the products of the reactions of B with C2H6, CH3NH2, and CH3OH, all of which are isoelectronic with CH3F. The calculations not only predict the vibrational frequencies exceptionally well, but also predict that there is no dative bonding in either CH2BX or CHBX, despite the empty p-orbital on B and the filled p-orbitals on the halogen atom.

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Final Technical Report to the AFOSR

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Reactions of Laser-Ablated Metal Atoms

September 1, 1998 to February 14, 2000

ACCOMPLISHMENTS

Research under Air Force support in the final year has involved reactions of laser-ablated metal atoms and hydrogen.

Reactions of laser-ablated ruthenium atoms with carbon monoxide and hydrogen in solid argon produce the unsaturated ruthenium carbonyl dihydride $H_2Ru(CO)_2$ and the hydrogen complexes $(H_2)_xRuCO$ (x=1,2). The observed absorption bands of the reaction products are identified by isotopic substitution and reproduced well by density functional theory calculations of vibrational fundamentals. The growth of bands due to $H_2Ru(CO)_2$ and $(H_2)RuCO$ during annealing in solid argon indicates that ruthenium monocarbonyl is coordinated with H_2 to form the dihydrogen complex $(H_2)RuCO$, while $H_2Ru(CO)_2$ is formed from the $(H_2)RuCO$ complex inserting into (H_2) upon coordinating with another CO.

Infrared spectra of representative LnH_{1-4} lanthanide hydride molecules are observed in solid argon following reactions of the laser-ablated metal atoms with H_2. The LnH_2 dihydride is

the major product. Spectra of isolated molecular EuH_2 and solid stoichiometric EuH_2 reveal close correspondence lending support to the molecular assignment, and by extrapolation, providing benchmark infrared frequencies for other lanthanide hydride solids based on their respective molecular vibrational modes.

Laser-ablated boron atoms react with methyl fluoride in an argon stream to form two major products, CH_2BF and CHBF. In similar reactions of boron with methyl chloride and methyl bromide, both CH_2BX and CHBX are also observed, as well as the primary insertion products, CH_3BCl and CH_3BBr, respectively. Infrared spectra of isotopic combinations of B and CH_3X and density functional theory frequency calculations provide evidence for the product identification. Both products form via insertion into the C-X bond followed by loss of one or two H atoms for all reactions. Comparisons are made with the products of the reactions of B with C_2H_6, CH_3NH_2 and CH_3OH, all of which are isoelectronic with CH_3F. The calculations not only predict the vibrational frequencies exceptionally well, but also predict that there is no dative bonding in either CH_2BX or CHBX, despite the empty p-orbital on B and the filled p-orbitals on the halogen atom.

PERSONNEL SUPPORTED

Xuefeng Wang and Stephen Willson

PUBLICATIONS

1. L. Andrews, P. F. Souter, W. D. Bare, and B. Liang, "Reactions of Laser-Ablated Mo and W Atoms with Dinitrogen: Infrared Spectra of Metal Nitrides, Dinitrides, and Complexes in Solid Argon and Nitrogen," *J. Phys. Chem. A* **1999**, *103*, 4649-4658.

2. L. Andrews, G. P. Kushto, M. F. Zhou, S. P. Willson, and P. F. Souter, "Infrared Spectrum of CCH^+ in Solid Argon and Neon," *J. Chem. Phys.* **1999**, *110*, 4457-4466.

3. S. P. Willson and L. Andrews, "Characterization of the Reaction Products of Laser-Ablated Lanthanide Metal Atoms with Molecular Hydrogen. Infrared Spectra of LnH, LnH_2, LnH_3, and LnH_4 Molecules in Solid Argon," *J. Phys. Chem. A* **2000**, *104*, 1640-1647.

4. X. Wang and L. Andrews, "Reactions of Laser-Ablated Ruthenium Atoms with CO and H_2 Mixtures: Infrared Spectra and Density Functional Theory Calculations of $H_2Ru(CO)_x$ (x=2-4) and $(H_2)RuCO$," *J. Phys. Chem. A* **2000**, in press.

5. D. V. Lanzisera and L. Andrews, "Reactions of Laser-Ablated Boron Atoms with Methyl Halides in Excess Argon. Infrared Spectra and Density Functional Theory Calculations on CH_3BX, CH_2BX and CHBX (X=F, Cl, Br)," *J. Phys. Chem. A* **2000**, in press.

INTERACTIONS

1. Invited Lecture: "Matrix Isolation – Past, Present, Future," Gordon Research Conference, Chemistry and Physics of Matrix Isolated Species, July 1999.

2. Invited Lecture: "Reactions of Laser-Ablated Transition Metal Atoms, Cations and Electrons with Small Molecules," Twelfth International Conference on Fourier Transform Spectroscopy, Waseda University, Tokyo, Japan, August 1999.

3. Visited Air Force Research Laboratories, host Dr. Mario Fajardo, November 19, 1999.